



Simulation insight into water transport mechanisms through multilayer graphene-based membrane



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ABSTRACT

Although single-layer nanoporous graphene has proven to be effective as a reverse osmosis desalination membrane, multilayer nanoporous graphene (MNPG) is economically affordable to be synthesized. In this study, water transport through large cylindrical (LC) and small cylindrical (SC), as well as through large hourglass-shaped (LHGS) pore structures constructed by MNPG is investigated via molecular dynamics (MD) simulations. It was found that the number of occupancy states increases with increasing pressure in LC pore, whereas they decrease with increasing pressure in SC pore. At $P = 2$ atm, water molecules must overcome a very large free energy barrier in SC pore owing to large entrance effects, suggesting a dramatic reduction in net flux. The LHGS pore structure is suggested to be a more efficient design for achieving higher flux, compared to other structures.

It was found that the hydrophilicity effect could nearly double the flux inside LHGS pore, owing to the strong hydrogen bonds. Moreover, the mean square displacement (MSD) profile in a hydrophilic pore shows larger displacement than a hydrophobic one, which facilitates water filling mechanism. It also indicated that the layers with hydrophilicity effect increase water concentration in the area close to the surface of the layers owing to strong hydrogen bonds. It is concluded that osmotic permeability of water molecules increases substantially inside hydrophilic LHGS pore.

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1. Introduction

Desalination is a viable solution to alleviate the global shortage of clean and fresh water. Developing energy-efficient and affordable technologies to desalinate seawater is rapidly becoming one of the most important research objectives of the 21st century. Membrane-type nanoporous materials have attracted considerable attention owing to their great potential for desalination. High selective water conduction can be achieved through narrow nanopores with ion passage blocked, and controlled by osmosis or reverse osmosis (RO). Carbon nanotube (CNT) arrays have been examined for desalination, by a charged end to repel positively charged particles so that uncharged water molecules can slip through the tubes, thereby reducing the pumping pressure. However, experiments and molecular dynamics (MD) [1,2] simulations have reported that CNTs allow fast water flow while providing low salt rejection. This seriously limits further applications of CNTs for improving desalination performance. Membrane separation based

on nanoporous graphene (NPG) has attracted substantial interest. Theoretical and experimental studies have reported that NPG membranes, primarily because of their thickness, are highly efficient for molecular separation, and RO desalination.

NPG, which is a one-atom-thick planar sheet, has a higher surface area and much more “space” for the transportation or storage of gas and liquid owing to the outstanding properties compared to ordinary graphene. Currently, microporous pores on graphene can be varied from 1 nm to several hundred nanometers by controlling temperature, diameter of nanorods, activation time and so on, based on different synthesizing methods including polymer building blocks [3–5], plasma-/electron-/photo-etching [6–8], template method [9–11], and chemical etching [12–14]. These methods pose challenge of precisely controlling the pore shape and size, and it is important to select a suitable method for large-scale and low-cost synthesis. A study [15] investigated water transport through a porous graphene membrane and compared the transport behavior with that through thin CNT membranes. For smaller diameter membranes, where single-file structure is observed, water flux through the graphene membrane is lower than that through the CNT membrane, primarily owing to the frequent rupture of the hydrogen bonding network and L/D defect-

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like water orientation in the graphene pore. On the other hand, for larger diameter pores, where the single-file structure is no longer observed, water flux through the graphene membrane is higher, than that of the CNT membrane, owing to the more bulky water neighbors and reduced permeation energy barrier at the entrance. NPG can be employed for membrane separation by drilling holes in single or few-layer graphene membranes [16]. Bio-mimetic membranes facilitate fast water conduction without permeation of ions, e.g., aquaporin water channels in cell membranes, which they allow water to flip through each 3 Å wide monomer with partial charged side chain inside, preventing the efficient transport of protons and ions [17].

Aquaporins (AQPs) have a homotetramer structure with each subunit having an hourglass shape. The unique shape of aquaporin water channels, suggesting an hourglass shape approximately 20 Å in length and 3 Å in the narrowest diameter at the center of the channel [17,18], plays a key role in fast water conduction. Understanding the mechanism of flow in aquaporin water channels can result in achieving high water permeation through semi-permeable membranes. Recently, an experimental study using transmission electron microscope (TEM) tomography [19] suggested that solid-state nanopores have an hourglass-shape than a cylindrical structure.

Some important physical characteristics of carbon-based aquaporin-like pores structures such as, single-file water structure, dipole reorientation, and osmotic permeability have been theoretically investigated by other researchers [20–24]. The results of these studies showed that a minimal departure from optimized cone angle significantly increased the osmotic permeability; and that there was a non-linear relationship between permeability and the cone angle. The observation of hydrophobicity effect on pore surface showed that the maximum water flux through an hourglass-shaped nanopore was at the hydrophobic state of $\theta_{\text{pore}} = 101^\circ$.

A MD study [25] showed that single layer NPG with functional group at the edge of pore, has great potential for desalination. This study also provided a method of estimating effective nanopore diameter by calculating the effective pore area. NPG continues to exhibit ultra-high water permeability, even at hydraulic pressures employed in reverse osmosis systems [26]. Results showed that the deformation at nanopore edge caused by high pressure may not seriously effect water flow across the nanopores. Another MD study [27] concluded that graphene membranes with non-functionalized (pristine) pores can be effectively used in water desalination only when the pores are very narrow. In that study, the effective pore diameter was 7.5 Å. The monolayer graphene is the thinnest material in nature, and it has great potential applications such as filtration and desalination. During filtration, the external pressure is exerted on the NPG membrane; therefore, the membrane should have enough load capacity to withstand the external pressure. A study [28] showed that the strength decreases as the size of the nanopore increases. An NPG membrane can maintain its mechanical integrity in RO system but the choice of substrate for graphene is critical to this performance. Cohen-Tanugi and Grossman [29], by using MD simulations and continuum fracture mechanics showed that an appropriate substrate with an opening smaller than 1 μm would allow NPG to withstand pressure exceeding typical pressure for seawater RO. Furthermore, they demonstrated that NPG membranes exhibit an unusual mechanical behavior in which greater porosity may help the membrane withstand even higher pressures. Most carbon-based nanochannels, such as CNTs, graphene, and graphene oxide laminates, contain a graphitic surface composed of many aromatic rings, which are hexagonal carbon rings rich in π electron [30]. Even though there is a weak interaction between aromatic rings and water molecules, the aromatic rings interplay strongly with

cation, which is referred to as cation-π interactions [31]. In the study of the mechanism of water molecules across the carbon-based nanochannels, cation-π interactions are generally not considered, whereas they play an important role in various systems and applications [32]. The non-covalent interaction between a cation and a π electron-rich carbon-based structure is termed the cation-π interaction [30]. Using density function theory (DFT) computations, Shi et al. [30] showed that large amounts of ions in the aqueous solution were absorbed by the carbon-based structure rich in π electrons. They concluded that Na⁺ is enriched on the typical hydrophobic carbon-based surface with the π electron-rich structures in aqueous salt solutions. Liu et al. [33] theoretically showed that water flow in narrow (6,6) CNTs was blocked by cations in the solution owing to the strong non-covalent cation-π interactions. They also suggested that by functionalizing the CNT entrance with saturated groups (-CH₂CH₂-) or applying an electric field along the channel the ion blocking could be prevented while attaining a fast water flow rate and 100% ion rejection. By employing the cation-π interactions, Shi et al. [34] concluded that the behavior of water molecules near aromatic rings is strongly affected by the presence of cations. Their results indicated that Na⁺ ions are attached to the aromatic rings on the graphene surface while retaining their hydration water molecules, resulting in the formation of molecular-thick pancakes of aqueous salt solutions on the graphene layers. For simplicity, we do not consider the cation-π interactions in this study, despite it being suggested that cation-π interactions have negligible effect on water molecules.

Recently, a study used MD simulation [35] to investigate the water transport and salt rejection mechanisms through the bilayer NPG membrane. They could successfully show the effects of layer separation, and pore alignment on desalination performance. Their results revealed that a bilayer NPG membrane can prove to be an effective RO membrane. In the current study, three simulation models including SC and LC pore systems in conjunction with LHGS pore structure are designed in MNPG. By utilizing the advantage of NPG, the study aims to investigate the effects of the pressure difference and the hydrophobicity/hydrophilicity on water transport through MNPG.

2. Simulation models and details

We performed MD simulations to investigate water transport through small cylindrical (SC) and large cylindrical (LC) pore structures and compared them with water transport through large hourglass-shaped (LHGS) pores in MNPG. Graphene samples (armchair) were generated using VMD Nanotube Builder. In reality, graphene sheets tend to form irreversible agglomerates or restack to graphite owing to strong π-π stacking and van der Waals interactions between the inter sheet of graphene. This problem can be solved by designing out-of plane space by introducing “spacers” between graphene layers, e.g., carbon black [36], carbon nanotubes [37–41], carbon nanofibers [42], metal oxides [43,44], and so on [45–49]. Instead of plugging in out-of-plane spacers to maintain constant distance between layers, the pristine NPG samples were artificially set to be frozen. The simulation model (31.9 × 34.3 × 51.0 Å³) contained bulk water regions surrounding a nanopore. SC and LC simulation models were constructed by assembling seven graphene monolayers with diameters of 3.1 and 4.4 Å, respectively, and for comparison, a large simulation model was symmetrically constructed by replicating the hourglass-shaped aquaporin water channel with diameter changing from 3.6 to 4.4 Å, as shown in Fig. 1. NPG layer was introduced by removing adjacent carbon atoms in the center of layer and selecting pores without sharp edges, after estimating the effective pore diameter d_{eff} using $d_{\text{eff}} = \sqrt{A_{\text{eff}}/\pi}/2Z$ [25]. The effective area

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